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# Installing Multiple Functional Groups on Biodegradable Polyesters via Post- Polymerization Olefin Cross Metathesis

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## **ABSTRACT**

Olefin cross metathesis is an effective tool for the functionalization of biodegradable aliphatic polyesters through both pre- and post-polymerization of  $\beta$ -heptenolactone ( $\beta$ HL). Ring opening polymerization of  $\beta$ HL accesses both homopolymers and novel copolymers, producing strong gradient copolymers with lactide. A total of 15 different alkene cross partners ranging from type I to type III olefins are readily incorporated to produce polyesters with a range of functionalities, altering the thermal and chemical

properties of the resulting polymers. A novel methodology was also developed to introduce two unique functionalities into the polymer backbone based on manipulation of cross-partner reactivity, showcasing the scope and versatility of olefin CM as a strategy for post-polymerization modification of polymers.

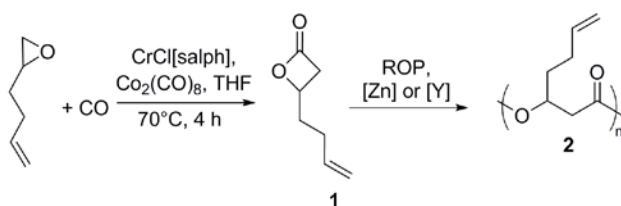
## INTRODUCTION

Biodegradable polyesters are of growing interest in both academia and industry, with poly(lactic acid) (PLA) serving as the most commercially relevant candidate due to its multiple applications as a commodity and specialty plastic.<sup>1-3</sup> PLA is routinely synthesized via the catalyzed ring-opening polymerization (ROP) of the cyclic monomer lactide (LA). This route boasts control and predictability over the molecular weight and dispersity ( $\mathcal{D}$ ) obtained, yet the thermal and physical properties of PLA are non-ideal.<sup>4</sup> Strategies are thus sought to overcome poor thermal performance and material brittleness challenges, including microstructure, comonomer and macrostructure solutions.<sup>5-12</sup>

Beyond lactide, poly(hydroxyalkanoates) (PHAs) are of growing interest. The most common of these is  $\beta$ -butyrolactone, of which homopolymers and copolymers with lactide are now well known.<sup>10,13-16</sup> Extending these efforts, our group recently reported the synthesis of well-defined ABA triblock polymers of lactide with substituted propiolactones with tunable thermal properties.<sup>16</sup> However, PHAs with pendent functional groups are far less explored. In particular, a paucity of reported research exists on  $\beta$ -heptenolactone,<sup>17-22</sup> ( $\beta$ HL, monomer **1**, Scheme 1), which when ring-opened affords a poly(hydroxyalkonate) bearing a pendent olefin arm (PHA<sup>olefin</sup>, polymer **2**, Scheme 1).

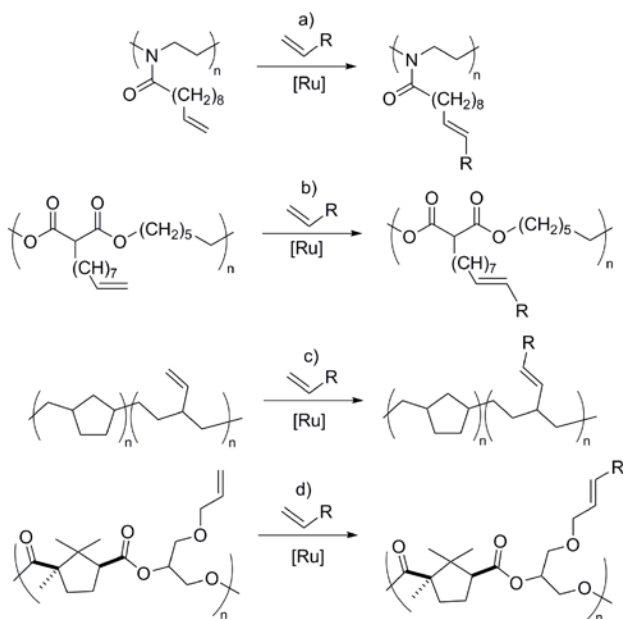
Alper *et al.* reported the first synthesis of **1** via the carbonylation of the parent epoxide using a cobalt based catalyst,<sup>20</sup> a method extended by Coates *et al.* who developed a more active chromium catalyst for efficient synthesis of the target monomer.<sup>22</sup> Reports of ring-opening polymerization of **1** are rare but include zinc<sup>23</sup> and yttrium<sup>24</sup> systems affording isospecific and syndiospecific polymers respectively.<sup>25</sup> While the pendent olefin arm provides access to a variety of post-polymerization modification strategies, only hydroboration has been reported to date.<sup>25</sup>

**Scheme 1.** Carbonylation and polymerization of  $\beta$ HL



A complementary approach to modify polymer **2** is olefin cross metathesis (CM). While ring opening metathesis polymerization (ROMP) and ring-closing metathesis (RCM) have both been highly successful in polymer synthesis, cross metathesis has only recently emerged as a potential candidate for polymer modification. Challenges with product selectivity and a negligible entropic advantage position CM as the least explored of the three transformations. However, active and robust Ru-based metathesis catalysts permit olefin CM to serve as a broad scope, functional group tolerant technique for post-polymerization modification.<sup>26,27</sup> Research in this area is very limited, both the use of olefin CM to directly functionalize polymer backbones<sup>28–39</sup> (Scheme 2) and as a diversification strategy for pre-polymerization metathesis of monomers.<sup>40–42</sup> Acrylates

tend to be the cross partner of choice in functionalizing the reported polymers, with little effort made to expand the scope of this potentially important reaction.



**Scheme 2.** Examples of post-polymerization functionalization via olefin cross metathesis by a) Hoogenboom,<sup>29</sup> b) Meier,<sup>32</sup> c) Coates<sup>38</sup> and d) Prunet and Thomas.<sup>39</sup>

Selected examples showing this limited scope include the following: i) methyl acrylate and ferrocenyl acrylate have been used to functionalize polyolefin dendrimers with 9-81 pendent allyl arms,<sup>30</sup> ii) a range of acrylates including methyl, tert-butyl, 2-hydroxyethyl and a PEG-substituted acrylate were used to functionalization poly(2-oxazoline)s<sup>29</sup> and poly(malonate)s,<sup>32</sup> and iii) the CM of homo- and co-polymers containing units of 3-vinyl tetramethylene with various acrylates was extended to 1-octene and 4-pentene-1-ol.<sup>38</sup> While we were developing this work for publication, Prunet and Thomas reported the tandem ROP of cyclic anhydrides with vinyl containing epoxides to generate a set of

novel copolymers that were modified with allyl acetate, methyl acrylate, styrene and allyl trimethylsilane.<sup>39</sup>

Herein we report pre- and post- polymerization metathesis of biodegradable polyester **2** and its novel copolymers with lactide. A broad substrate scope of 15 different cross metathesis partners is developed to give a novel set of polymers with tunable properties. Importantly, exploiting CM reactivity trends affords a route to incorporate two unique functionalities into the same polymer chain and is the first example of double metathesis in polymer functionalization.

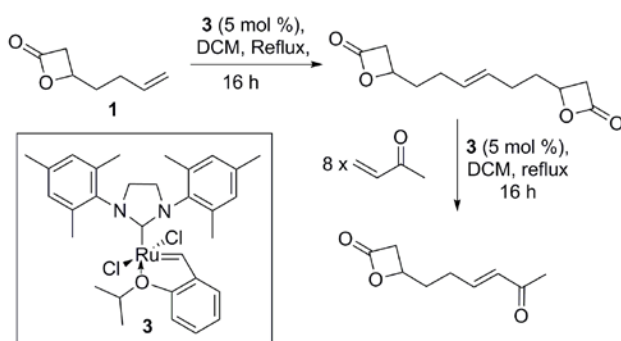
## RESULTS AND DISCUSSION

Two routes to CM-derived functional aliphatic polyesters were explored, both built from the same olefin-functionalized lactone. **1** was prepared in good yields and short reaction times via the carbonylation of 1,2-epoxy-5-hexene using [salph(Cr(THF)<sub>2</sub>)[Co(CO)<sub>4</sub>], as reported previously.<sup>22</sup> Initially, pre-polymerization CM of monomer **1** was targeted to generate a library of functionalized monomers. A potential benefit of this approach is that it provides a simple route to polymers with absolute control over functional group incorporation.

Selectivity is a particular challenge in olefin CM. To help predict olefin reactivity Grubbs proposed an empirical model that categorizes olefins into four different types based on their ability to undergo homodimerization and for these homodimers to undergo secondary metathesis reactions in the presence of commercially available catalysts.<sup>43</sup>

Electron rich, sterically unhindered olefins are reactive and categorized as type I olefins, while electron deficient, sterically hindered olefins are unreactive and categorized as type IV olefins. To experimentally identify the reactivity category of monomer **1**, a self-metathesis reaction using Hoveyda-Grubbs second generation catalyst, **3**, was conducted (Scheme 3). Successful self-metathesis was evidenced by disappearance of the original alkene protons in the NMR spectrum (Figure S1). This self-metathesis product was then subjected to a second metathesis reaction with a less reactive type II olefin, 3-butene-2-one. Successful CM with >95% incorporation of the cross partner supports the classification of monomer **1** as a type I olefin.

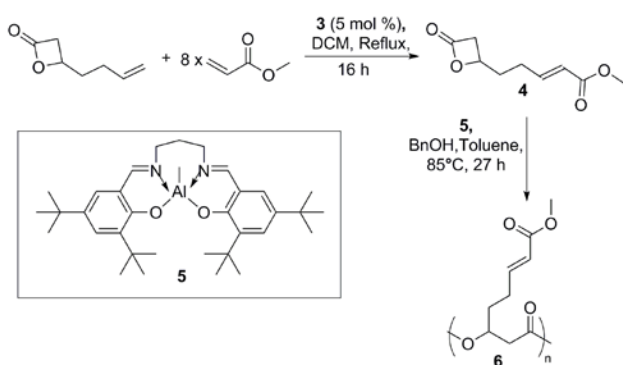
**Scheme 3.** Olefin categorization of  $\beta$ HL



The high reactivity of monomer **1** enabled metathesis with a wide scope of substrates ranging from type I to type III olefins (Figure S2). To ensure a high level of functional group incorporation, a large excess of the cross partner was used. While CM was successful, as evidenced by NMR spectroscopy (Figure S3), purification of the novel monomers was challenging. Column chromatography was problematic due to the similar retention times of the different combination of metathesis products obtained. While not readily scalable, two successive column purifications did lead to successful isolation of

monomer **4** in high regioselectivity (*trans:cis*, 97:3), resulting from the CM reaction of monomer **1** with methyl acrylate (Scheme 4, Figures S4-S7). Ring opening polymerization of **4** was mediated by an aluminium salen catalyst (**5**, Scheme 4). This catalyst has shown a very high monomer scope in controlled ROP, including both lactide and a variety of substituted propiolactones.<sup>44-46</sup> Polymerization of **4** is slow, like other long chain propiolactones, and reaches 93% conversion in 27 hours at 85°C to give polymer **6** (Scheme 4, Figure S8).

**Scheme 4.** Metathesis of  $\beta$ HL and successive ring-opening polymerization



Molecular weights were low ( $M_n = 2,400$ ) relative to that predicted by monomer conversion ( $M_{n,th} = 18,400$ ) and the  $\mathcal{D}$  was broad ( $\mathcal{D} = 1.65$ ). We reasoned this was a result of competing coordination and transesterification of the acrylate functionality to the Lewis acidic aluminum center, thereby suppressing the control. While this result marks one of a few examples of cross metathesis pre-polymerization functionalization of a biodegradable monomer, challenges with both polymerization control, long reaction times and challenging monomer purification led us to pursue a more accessible strategy to prepare functional aliphatic polyesters.



Our second, and preferred, strategy involved post polymerization metathesis of polymer **2** which was synthesized via the ring opening polymerization of monomer **1** using Al(salen) complex **5** (S9-12). In contrast to monomer **4**, the polymerization was very well controlled, as demonstrated by its low Đ (1.09) and predictable molecular weights. Kinetic data indicates the reaction follows first order kinetics for monomer conversion, typical of a controlled polymerization (Figure S13). From **2**, olefin CM was initially tested using two different olefin cross partners: methyl acrylate (a type II olefin) and 1,2-epoxy-5-hexene (a type I olefin) (Table 1).

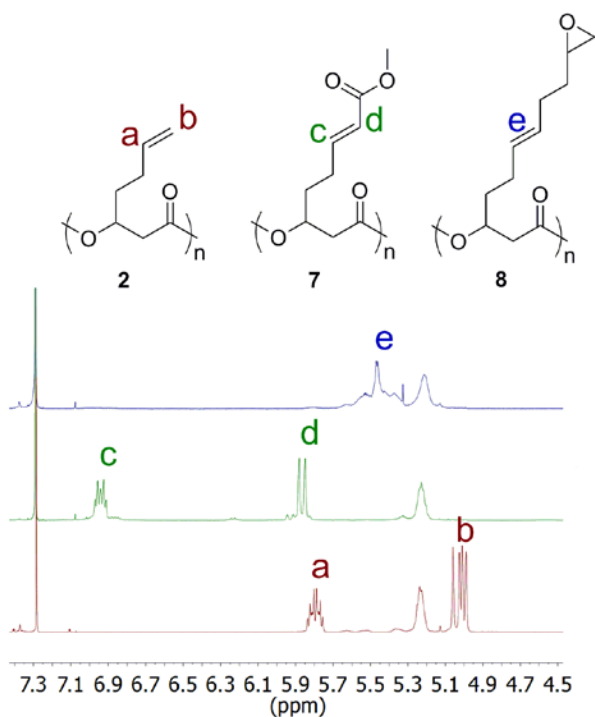
**Table 1.** Post-polymerisation metathesis of PHA<sup>olefin</sup>

Polymer		Conv. (%) <sup>a</sup>	M <sub>n</sub> , <sup>b</sup>	Đ <sup>b</sup>
2	None	>99	12,100	1.092
7		>99	13,400	1.842
8		>99	11,300	1.423

<sup>a</sup>Determined by NMR. <sup>b</sup> Determined by GPC analysis, conventional calibration uncorrected vs polystyrene standards.

CM of **2** with methyl acrylate gave complete incorporation of the new functionality into the polymer backbone as verified by NMR spectroscopy (**7**, Figure 1, Figures S14-17). Complete consumption of the original alkene protons and growth of new alkene protons

were observed alongside a small portion of *cis*-product. Isolation of the resulting polymer was much easier than that of the functionalized monomer **4**. While precipitation was not possible for the oily, low  $T_g$  polymer, **7** was readily purified by column chromatography. The molecular weight obtained from GPC indicated a negligible increase in molecular weight distribution versus uncorrected polystyrene standards, compared to the non-functionalized precursor, a result seen previously in the literature.<sup>39</sup> CM of polymer **2** with 1,2-epoxy-5-hexene was also successful, as confirmed by NMR spectroscopy, with >90% incorporation of the target functional group (**8**, Figure 1, Figures S18-21). Once again, the observed  $M_n$  showed a negligible change by GPC.

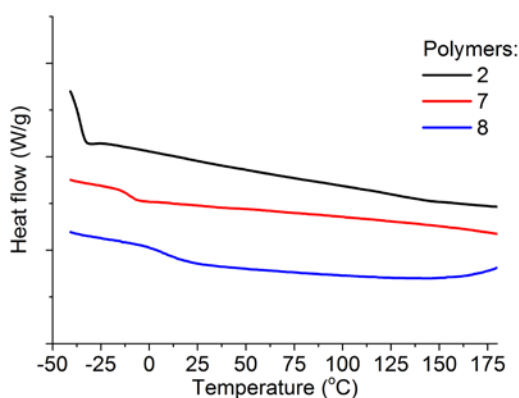


**Figure 1.**  $^1\text{H}$  NMR for metathesis products

However, in both **7** and **8** a noticeable increase in  $\bar{M}_w$  was observed, suggesting a small amount of cross-linking may be occurring, that was undetected by NMR analysis. With

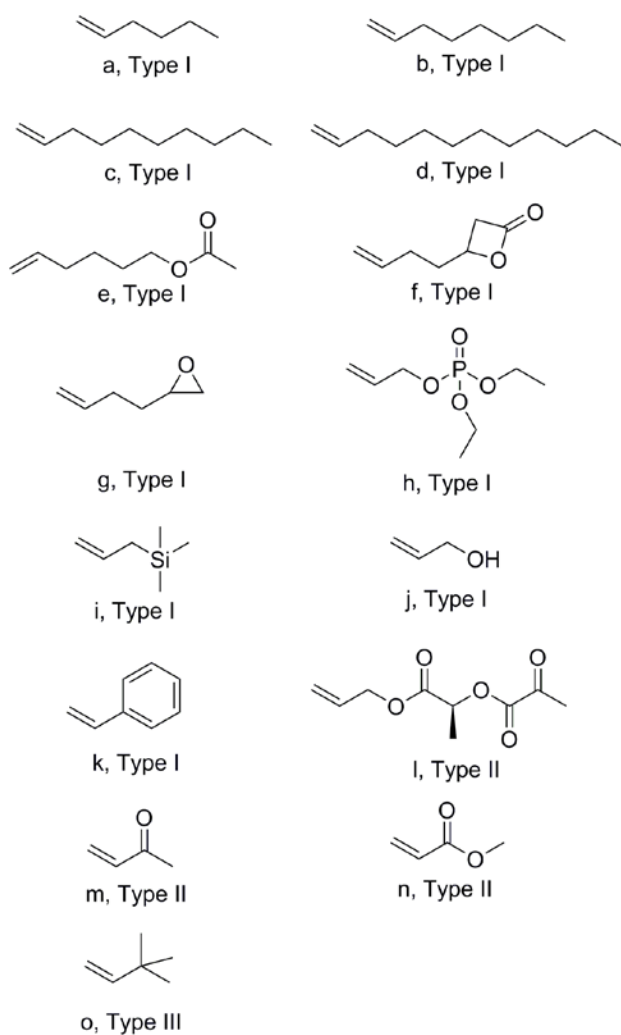
the knowledge that monomer **1** was able to homodimerize, we investigated the ability of **2** to undergo self-metathesis. As expected, the reaction formed an insoluble cross-linked network that we were unable to analyze by conventional means. This suggests that the high loading of olefin cross partner drives the reaction to the desired product and limits cross-linking.

To further understand the significance of functional group incorporation, thermal analysis was performed to compare the properties of the newly functionalized polymers. Thermal gravimetric analysis (TGA) indicates that the incorporation of the two functional groups significantly impacts thermal stability (Figure S22). Functionalizing **2** induces a significant decrease in onset degradation temperatures:  $T_{5\%}$  decreases by 49°C for methyl acrylate and 35°C for epoxide functionalized polymers. Derivative thermogravimetry (Figure S23) highlights the temperature at which degradation rate is fastest,  $T_{\max}$ , which also decreases by 39°C and 25°C for polymers **7** and **8** respectively. Functional group incorporation also has a substantial impact on the glass transition temperatures ( $T_g$ ) of the resulting polymers, increasing the  $T_g$  of **2** (-38°C) by 25°C and 48°C for the acrylate and epoxide derivatives (Figure 2).



**Figure 2.** DSC of polymers **2**, **7** and **8**

While these results are promising, we recognize the inherent challenge in developing new polymers from expensive monomer feedstocks. Our pursuit of more sustainable functional polyesters would thus target strategies where the bulk of the polymer is derived from a renewable, inexpensive source. We thus investigated the copolymerization of monomer **1** with lactide (LA), forming a copolymer with a controllable percentage of functional groups modifiable by post polymerization metathesis. This would enable a viable route to introduce functionality into PLA to target specialty applications. As the rate of polymerization of LA is much faster than **1** (Figure S24), a gradient copolymer is expected to be formed upon simultaneous monomer addition. We prepared two copolymers with different monomer ratios in the polymer backbone (**1** : LA 4:87 to produce polymer **9**) and (**1** : LA, 19:85 to produce polymer **11**), the first such examples of copolymers with **1** (Figures S25-28). Post polymerization metathesis was highly successful, permitting a large substrate scope to be explored (Figure 3, Table 2).



**Figure 3.** Olefin cross partners coupled to **9** and **11** to afford **10a-o** and **12a-o**.

**Table 2.** Post-polymerization metathesis of copolymers of LA and  $\beta$ HL

<p><b>9</b> (n= 86, m= 4)  <b>11</b> (n= 85, m= 19)</p> <p><b>10a-o</b> (n= 86, m= 4)  <b>12a-o</b> (n= 85, m= 19)</p>									
Polymer		Conv. <sup>a</sup> (%)	M <sub>n</sub> <sup>c</sup>	Đ <sup>c</sup>	T <sub>5%</sub> <sup>d</sup> (°C)	T <sub>max</sub> <sup>d</sup> (°C)	T <sub>g</sub> <sup>e</sup> (°C)	T <sub>c</sub> <sup>e</sup> (°C)	T <sub>m</sub> <sup>e</sup> (°C)
9			12,000	1.02	308	352	55	90	157

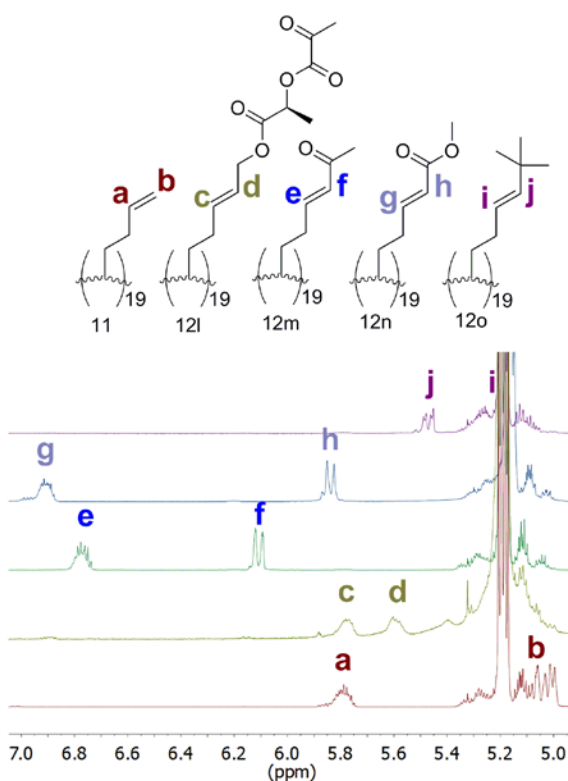
10a	a	n.d <sup>b</sup>	14,800	1.02	304	360	54	92	156
10b	b	n.d <sup>b</sup>	22,000 <sup>f</sup>	1.47 <sup>f</sup>	302	362	54	90	157
10c	c	n.d <sup>b</sup>	11,400	1.02	308	368	55	88	157
10d	d	n.d <sup>b</sup>	12,700	1.06	287	351	51	86	157
10e	e	n.d <sup>b</sup>	12,300	1.03	n.d	n.d	50	82	157
10f	f	n.d <sup>b</sup>	14,000	1.03	262	369	54	91	156
10g	g	n.d <sup>b</sup>	20,500 <sup>f</sup>	1.33 <sup>f</sup>	226	364	55	93	157
10h	h	n.d <sup>b</sup>	12,300	1.01	317	370	54	89	157
10i	i	n.d <sup>b</sup>	13,900	1.02	215	371	57	93	158
10j	j	n.d <sup>b</sup>	16,400	1.42	n.d	n.d	57	91	156
10k	k	n.d <sup>b</sup>	13,000	1.04	308	370	59	93	157
10l	l	n.d <sup>b</sup>	16,200	1.20	304	367	57	94	156
10m	m	n.d <sup>b</sup>	17,300	1.01	310	371	n.d.	n.d.	n.d.
10n	n	n.d <sup>b</sup>	16,800	1.07	305	370	53	n.o	157
10o	o	n.d <sup>b</sup>	12,300	1.04	295	365	n.d.	n.d.	n.d.
11			9,500	1.04	293	345	45	94	134
12a	a	>95	n.d	n.d	272	361	43	94	136
12b	b	76	9,900	1.03	274	358	40	93	134
12c	c	87	10,400	1.04	n.d	n.d	n.o	95	137
12d	d	87	11,300	1.18	277	359	37	92	134
12e	e	55	10,700	1.04	278	360	40	93	134
12f	f	74	16,100	1.98	267	344	47	99	139
12g	g	>99	11,600	1.08	236	343	44	97	138
12h	h	76	9,600	1.06	286	364	45	97	136
12i	i	n.d	9,300	1.04	280	361	46	97	136
12j	j	n.d	29,400	4.25	295	351	54	111	143
12k	k	71	12,600	1.24	266	360	53	104	139
12l	l	>99	23,800	2.39	233	362	49	n.o	n.o
12m	m	>99	9,800	1.03	299	355	48	101	139
12n	n	>99	12,100	1.02	297	350	46	98	136
12o	o	>99	8,000	1.05	294	359	50	101	137

<sup>a</sup>Determined by NMR integration. <sup>b</sup>Incorporation too low to determine by NMR. <sup>c</sup>Determined by triple detection GPC analysis. <sup>d</sup>Determined by thermal gravimetric. <sup>e</sup>Determined by differential

scanning calorimetry. <sup>f</sup>Determined by conventional calibration uncorrected vs polystyrene standards. n.o = not observed. n.d = not determined.

The scope of the metathesis reaction was investigated under standard conditions (5 mol% **3**, 16 h, DCM) with a wide range of olefin cross partners from type I to type III (Table 2). The olefins include a wide range of functional groups including silane, phosphonate, acrylate, aromatic and aliphatic groups. Less reactive type II and type III olefins gave full incorporation (Figure 4, Table 2, **12l-12o**) due to their slow rates of homodimerization (See Figures S29-30 for analysis of novel alkene **1**. This alkene is able to homodimerise and due to its similar reactivity trend to the other type II and III olefins it is assumed a type II). The remaining alkene cross partners, more reactive type I olefins, give incomplete incorporation of the functional group into the polymer backbone. These polymers (**12a-12k**) can be isolated and subjected to a second metathesis with the same alkene partner at an increased catalyst loading of 10 mol%, with the hope to drive the reaction to completion. Under these conditions, polymers **12a** and **12g** can be formed with >99% functionality incorporation. The remaining polymers all contain a persistent parent alkene component, ranging from 10-40% depending upon the functional group. We hypothesize that this feature results from competition between the different CM reactions accessible; the rate of selective cross metathesis competes with the rate of homodimerization of the alkene cross partner which competes with the rate of secondary metathesis of the functionalized copolymers. It is also important to note that steric hindrance associated with the alkene cross partners may also play a role in incomplete functionalization, by subsequently blocking access to the free alkene on the polymer backbone. Further optimization of conditions including the ratio of olefin cross partner, the catalyst loading and the reaction temperature have little effect (Table S1). As seen

with the homopolymers there is no observable increase in molecular weight by GPC. The low percentage incorporation of monomer **1** in polymer **9** also makes it difficult to accurately quantify incorporation of the functional groups by NMR integration (**10a-10o**), and all values presented are best estimates from peak integration (**12a-12o**). Most polymers show exceptionally low dispersities, although some cross-linking is evident in **12j** and **12l**; this is possible by the large excess of coupling partner, as **9** forms an intractable gel in the absence of added olefin.



**Figure 4.** NMR spectra of CM products of copolymers.

A clear change is observed, however, in the thermal properties of polymer families **10** and **12** (Table 2). As expected, the larger incorporation of functional groups in polymers **12a-o** induce a greater shift in the thermal properties (Figures S31-36). The incorporation of functional groups does not significantly affect observed  $T_m$ s. Incorporation of allyl

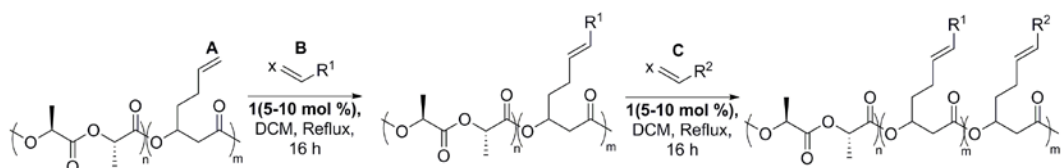



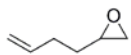
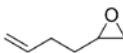


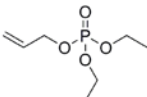

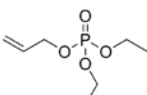

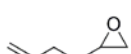

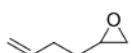
alcohol (**12j**) and styrene (**12k**) increase  $T_g$ s by 9°C and 8°C, respectively, and  $T_c$ s by 17°C and 10°C, perhaps promoted by hydrogen bonding or  $\pi$ - $\pi$  interactions in the two systems. A dramatic decrease in  $T_{5\%}$  for polymer **10i** containing allyl silane was observed, dropping by 93°C from 308°C to 215°C.

While an incomplete incorporation of the desired functional group may seem detrimental, it offers access to arguably the most interesting feature of our system. We considered the possibility of using double metathesis as a simple yet novel route to introducing two different functionalities into the same polymer backbone. To develop this strategy we exploited the difference in reactivity of the olefin cross partners. As cross metathesis of type II and type III olefins reach completion, we coupled these with more reactive type I olefins in a double CM. Results are shown in Table 3 and highlight the importance of order of addition in achieving double functionality. Comparing polymer **13** to **14** show it is critical to react the polymer with the type II methyl acrylate first followed by reaction with the more reactive type I olefin, 1,2-epoxy-5-hexene second. NMR spectra confirm incorporation of both functionalities into the backbone to produce **13** (Figure 5) and suggests the rate of secondary metathesis of the functionalized polymer bearing methyl acrylate is slower than the rate of homodimerization of the epoxide. Reversing the order of addition simply results in full incorporation of methyl acrylate (**14**) indicating this time that the rate of secondary metathesis of the functionalized polymer bearing the epoxide is faster than the rate of homodimerization of methyl acrylate. Polymer **15** incorporates predominantly the type I phosphorous functionality. This highlights the nuances that exist within the different olefin categories: Both allyl phosphonate and 1,2-epoxy-5-hexene are

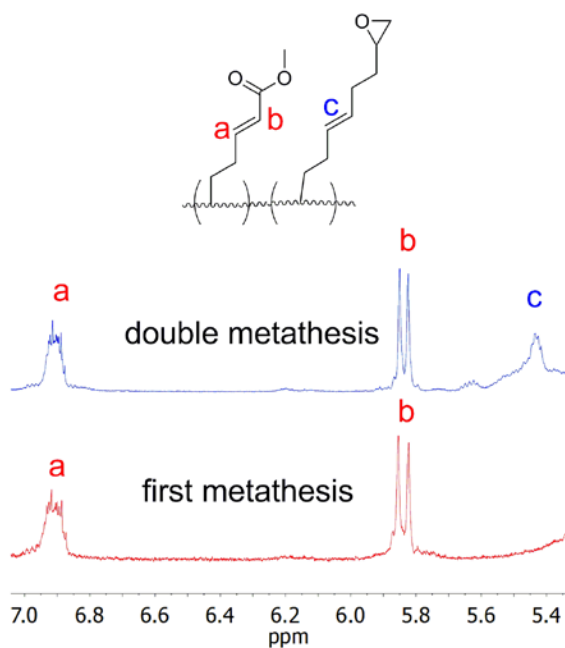
categorized as reactive type I olefins, yet the epoxide has a greater affinity to homodimerize compared to allyl phosphonate, likely due to the greater steric hindrance of allyl phosphonate. Lowering the ratio of allyl phosphonate results in less secondary metathesis of the polymer functionalized fully with methyl acrylate, thus affording the desired polymer **16**. Finally, we explored the ability of type III olefin, 3,3-dimethyl-1-butene, to undergo double metathesis in the presence of reactive type I olefin 1,2-epoxy-5-hexene, giving no incorporation of the epoxide into the polymer backbone (**18**). This indicated the combination of the type III olefin with the polymer must generate an unreactive type IV species unable to undergo secondary metathesis with the epoxide. Thermal properties are shown in Table 4 but are unremarkable (Figures S37-39).

**Table 3.** Double CM on copolymers of LA and  $\beta$ HL



Polymer.	B	Eq	% A remaining <sup>a</sup>	C	Eq	A:B:C <sup>a</sup>
13		1	13		8	0:1:0.78
14		12	13		5	0:0:1
15		1	18		5	0:0.36:1
16		8	0		0.3	0:1:0.25
17		8	6		0.3	0.26:0.9:1
18		8	0		0.3	0:1:0

<sup>a</sup>Determined by NMR spectroscopy.



**Figure 5.** NMR of double CM, polymer **13**

**Table 4.** Thermal properties of double CM

Polym.	$M_n^a$	$\bar{D}^a$	$T_{5\%}^b$ (°C)	$T_{max}^b$ (°C)	$T_g^c$ (°C)	$T_c^c$ (°C)	$T_m^c$ (°C)
19 <sup>d</sup>	10,400	1.03	289	342	43	97	135
13	20,700	1.25	290	355	46	101	137
20 <sup>d</sup>	9,800	1.02	301	350	44	93	133
16	22,000	2.34	288	368	49	102	140
17	21,200	1.76	291	364	51	103	140

<sup>a</sup>Determined by triple detection GPC analysis. <sup>b</sup>Determined by thermal gravimetric analysis. <sup>c</sup>Determined by differential scanning calorimetry. <sup>d</sup>Copolymers prior to metathesis.

This strategy for two successive metathesis reactions represents a novel route of introducing double functionality into a polymer backbone. To the best of our knowledge this is the first example to exploit difference in reactivity levels of olefin cross partners in order to incorporate two unique functionalities into a polymer. With further optimization a variety of polymer architectures ranging from gradient to various block polymers with targeted thermal properties can be achieved using this new methodology and represents a significant current research effort in our group.

## CONCLUSIONS

In summary, we have showcased the scope of CM reactions in designing functional polymers. Pre-polymerization metathesis using monomer  $\beta$ HL with methyl acrylate is successful, but requires complicated monomer purification. Post-polymerization metathesis is efficient for homopolymers of  $\beta$ HL, affording methyl acrylate and 1,2,-epoxy-5-hexene functionalized polyesters. The first reported co-polymers of LA and  $\beta$ HL were synthesized and used in successful post-polymerization metathesis, with a wide substrate scope ranging from type I to type III olefins, to readily access a large family of PLA derivatives. To our knowledge, this is the first report of post-polymerization metathesis exploring such an array of cross partners. Moreover, an operationally simple method to incorporate two distinct functionalities into these copolymers has been developed, tuned by the inherent reactivity of the cross partners incorporated. Our current efforts explore the control and selectivity of the cross partners during double metathesis and extend this work to other polymer architectures.

## EXPERIMENTAL

### General Methods

Experiments involving air and moisture-sensitive compounds were either performed under a nitrogen atmosphere using an MBraun LABmaster sp glovebox system equipped with a  $-35\text{ }^{\circ}\text{C}$  freezer and  $[\text{H}_2\text{O}]$  and  $[\text{O}_2]$  analyzers or using standard Schlenk techniques. Dichloromethane (DCM), tetrahydrofuran (THF) and toluene were obtained from an Innovative Technologies solvent purification system incorporating columns of alumina and copper catalysts and were de-gassed by three freeze-pump-thaw cycles prior to use.  $\text{MeAl}[\text{salen}]^{\text{tBuPr}}$ ,  $\text{ClCr}[\text{salph}]$  and 3-methylene-6-methyl-1,4-dioxane-2,5-dione were synthesised via literature procedures. Carbon monoxide (99.9%, BOC) was used as received. L-Lactide was purified via vacuum sublimation and dried under reduced pressure for 16 h. Benzyl alcohol was dried over calcium hydride for 24 h under reflux, distilled under nitrogen and degassed by three- freeze-pump thaw cycles. Hoveyda-Grubbs second generation catalyst, diethyl allyl phosphonate and 3-butene-2-one were purchased from Sigma Aldrich. 1,2-Epoxy-5-hexene, allyl alcohol, allyltrimethylsilane, 3,3-dimethyl-1-butene, 1-octene and dicobalt octacarbonyl were purchased from Acros Organics. 1-Decene, 5-hexenyl acetate and methyl acrylate were purchased from Alfa Aesar. 1-Dodecene and styrene were purchased from Merck Millipore. All chemicals were used as received except alkenes which were dried over calcium hydride for 24 hrs

and either distillation or vacuum transfer under a nitrogen atmosphere was used prior to being de-gassed by three freeze-pump-thaw cycles.

## **Characterization**

Gel permeation chromatography (GPC) was performed using a Malvern Instruments Viscotek 270 GPC Max triple detection system with  $2 \times$  mixed bed styrene/DVB columns ( $300 \times 7.5$  mm) in THF at a flow rate of  $1 \text{ mL min}^{-1}$  and an injection volume of  $200 \mu\text{l}$ . Samples for analysis were pre-dissolved in chloroform at a concentration of  $\sim 8\text{--}12 \text{ mg/ml}$ .  $^1\text{H}$  NMR spectra were recorded at 298K using BrukerAsance spectrometers (400, 500 or 600 MHz).  $^{13}\text{C}$  NMR spectra were recorded using BrukerAsance spectrometers (126 MHz). 2D NMR analyses (COSY, HSQC and HMBC) were recorded using BrukerAsance spectrometers (500 or 600 MHz).  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum was obtained using a BrukerAsance spectrometer (202 MHz).  $\text{CDCl}_3$  or  $\text{C}_6\text{D}_6$  were used as solvents for all NMR analyses. Differential scanning calorimetry (DSC) was carried out using a TA Instruments DSC Q2000 instrument, through a heat/cool/heat cycle between  $-90^\circ\text{C}$  to  $200^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$ . Values of  $T_g$ ,  $T_m$  and  $T_c$  were obtained from the second heating scan. Thermogravimetric analysis (TGA) measurements were performed on a SDTQ600. Samples were heated from room temperature to  $800^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$  using recycled pans.

## **Synthesis of Monomer 4**

A solution of  $\beta$ HL (0.3 g, 2.4 mmol), methyl acrylate (1.64 g, 19 mmol) and Hoveyda Grubbs Second generation catalyst (0.0745 g, 0.12 mmol) in DCM (2 ml) was sealed in an oven dried ampoule. The solution was degassed by one freeze-pump-thaw cycles and heated under reflux for 16 h. The crude product was purified using column chromatography on silica gel (EtOAc:hexane, 10:90) followed by a second column (EtOAc:DCM 10:90) to afford the product as a yellow oil (0.14g, 32%).

### **Synthesis of Polymer 6**

Monomer **2** (0.09 g, 0.489 mmol)  $\text{MeAl}[\text{salen}]^{\text{tBuPr}}$  (0.0027 g,  $4.89\text{E}^{-3}$  mmol) and benzyl alcohol ( $5.288\text{E}^{-4}$  mmol) were dissolved in toluene (0.5 ml) and added to an oven-dried ampoule. The mixture was heated at 85°C for 27 h and quenched with the addition of a few drops of methanol. . The product was concentrated under reduced pressure to yield a dark brown oil.

### **Synthesis of olefin-polyhydroxyalkonate ( $\text{PHA}^{\text{olefin}}$ ), Polymer 2**

$\beta$ HL (3 g, 23.8 mmol),  $\text{MeAl}[\text{salen}]^{\text{tBuPr}}$  (0.130 g, 0.238 mmol) and benzyl alcohol (0.0257 g, 0.238 mmol) were dissolved in toluene (1 5ml) and added to an oven-dried ampoule. The mixture was heated at 85°C for 27 h and quenched with the addition of a few drops of methanol. The product was concentrated under reduced pressure to yield a light brown oil.

### **Post-polymerisation Metathesis of Polymer 2**

A solution of **2** (0.250 g), alkene cross partner; methyl acrylate (1.7 g, 19.8 mmol) or 1,2-epoxy-5-hexene (1.943 g, 19.8 mmol) and Hoveyda Grubbs second generation catalyst

(0.124 g, 0.1982 mmol) in DCM (4 ml) were sealed in an oven dried ampoule. The solution was degassed by one freeze-pump-thaw cycles and heated under reflux for 16 h with occasional de-gassing. The crude polymer was purified using column chromatography on silica gel (DCM) to elute non-polymer alkene products. The polymer was then extracted from the silica using methanol washings and was filtered to yield the product as a dark brown oil.

### Synthesis of Alkene I

A solution of 3-methylene-6-methyl-1,4-dioxane-2,5-dione (0.5 g, 3.52 mmol) and methanol (0.135 g, 4.22 mmol) in DCM (3 ml) in an oven dried ampoule was degassed by three freeze-pump-thaw cycles. The solution was heated to 85°C for 24 hrs. The crude product was distilled under vacuum to afford the product as a colourless oil.

### Co-polymerisation of L-lactide and $\beta$ -heptenolactone

**L-lactide: $\beta$ HL (87:4) polymer 9;**  $\beta$ HL (0.39 g, 3.1 mmol), L-lactide (4 g, 28 mmol), MeAl[salen]<sup>tBuPr</sup> (0.169 g, 0.31 mmol) and benzyl alcohol (0.034 g, 0.31 mmol) were dissolved in toluene (20 ml) and added to an oven-dried ampoule. The mixture was heated at 85°C for 2.5 h and precipitated in cold methanol. **L-lactide:  $\beta$ HL (85:19) polymer 10;**  $\beta$ HL (1.44 g, 11 mmol), L-lactide (3.5 g, 24 mmol), MeAl[salen]<sup>tBuPr</sup> (0.156 g, 0.28 mmol) and benzyl alcohol (0.031 g, 0.28 mmol) were dissolved in toluene (20 ml) and added to an oven-dried ampoule. The mixture was heated at 85°C for 2.5 h and precipitated in cold methanol. . For analysis of **polymer 9** see NMR data of **polymer 11**.

### Representative Cross metathesis of Co-Polymers 9 and 11



Copolymer, alkene cross partner and Hoveyda Grubbs second generation catalyst were dissolved in DCM in an oven dried ampoule. The mixture was degassed by one freeze-pump-thaw cycle and heated for 16 h under reflux with occasional de-gassing. The reaction was quenched with a few drops of ethyl vinyl ether, precipitated in cold methanol and washed with cold diethyl ether and hexane. Polymers **12a-12k** were subjected to a second CM using the same alkene cross partner with a catalyst loading of 10 mol %.

For example: Copolymer (85:19) (0.1 g), 1-hexene (0.09 g, 1.08 mmol) and Hoveyda Grubbs second generation catalyst (0.0042 g,  $6.74\text{E}^{-3}$  mmol) were dissolved in DCM (2 ml) in an oven dried ampoule. The mixture was degassed by one freeze-pump-thaw cycle and heated under reflux for 16 h with occasional de-gassing. The reaction was quenched with a few drops of ethyl vinyl ether and precipitated in cold methanol (~20 ml) and washed with cold diethyl ether (~20 ml) and cold hexane (~20 ml). See SI for full characterisation (Figures S40-S98).

### **Representative Post-polymerisation Double Metathesis of Co-Polymers**

Copolymer, alkene cross partner one and Hoveyda Grubbs second generation catalyst were dissolved in DCM in an oven dried ampoule. The mixture was degassed by one freeze-pump-thaw cycle and heated for 16 h under reflux with occasional de-gassing. The reaction was quenched with a few drops of ethyl vinyl ether, precipitated in cold methanol and washed with cold diethyl ether and hexane. The functionalised polymer, alkene cross partner two and Hoveyda Grubbs second generation catalyst were dissolved in DCM in an oven dried ampoule. The mixture was degassed by one freeze-pump-thaw

cycle and heated for 16 hrs under reflux with occasional de-gassing. The reaction was quenched with a few drops of ethyl vinyl ether, precipitated in cold methanol and washed with cold diethyl ether and hexane.

For example, Polymer **13**: Copolymer (85:19) (0.2 g), methyl acrylate (0.023 g, 0.27 mmol) and Hoveyda Grubbs second generation catalyst (0.00844 g, 0.013 mmol) were dissolved in DCM (1 ml) in an oven dried ampoule. The mixture was degassed by one freeze-pump-thaw cycle and heated for 16 h under reflux with occasional de-gassing. The reaction was quenched with a few drops of ethyl vinyl ether, precipitated in cold methanol (~20 ml) and washed with cold diethyl ether (~20 ml) and hexane (~20 ml). The functionalised polymer (0.12 g), 1,2-epoxy-5-hexene (0.13 g, 1.3 mmol) and Hoveyda Grubbs second generation catalyst (0.01 g, 0.016 mmol) were dissolved in DCM (0.5 ml) in an oven dried ampoule. The mixture was degassed by one freeze-pump-thaw cycle and heated for 16 h under reflux with occasional de-gassing. The reaction was quenched with a few drops of ethyl vinyl ether, precipitated in cold methanol (~20 ml) and washed with cold diethyl ether (~20 ml) and hexane (~20 ml). See SI Figures S99-S100.

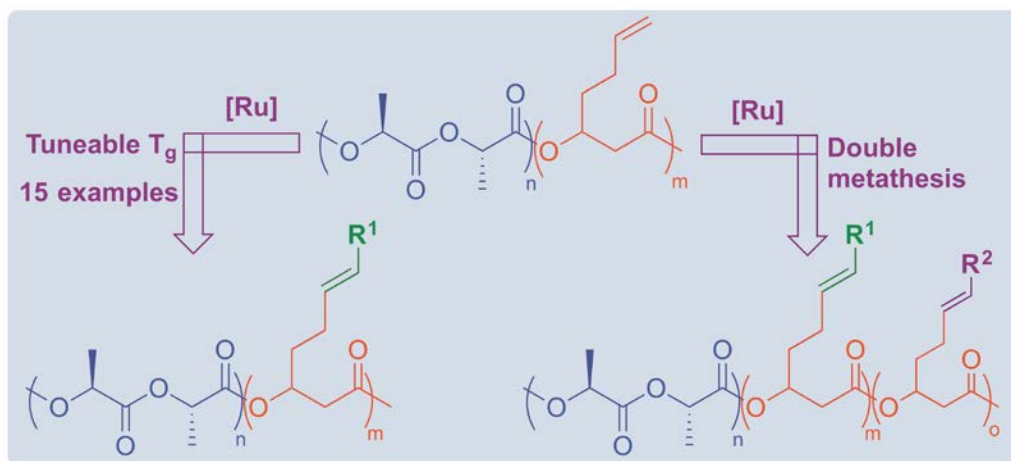
## **ASSOCIATED CONTENT**

**Supporting Information:** NMR shifts, spectra, kinetic plots, mass spectrometry and thermal analysis data associated with monomers, homo-polymers, co-polymers and all associated metathesis products.

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